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BENCH SCALE RETORTING OF KENTUCKY OIL SHALE: COMPARISON OF
A FIXED BED TO 1 1/2 AND 3 INCH FLUID BED RETORTS

By

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INTRODUCTION

Oil yields substantially in excess of Fischer Assay have been obtained for eastern U. S. oil shales by several different retorting technologies (1-5). The possibility of oil yield enhancement has now been confirmed by a number of researchers at different laboratories. However, the emphasis of most of the available information in the literature to date has been the determination of the maximum oil yield possible from eastern shales. The problem of how retorting under conditions such as fast heating, steam, sweep gases, or vacuum in a fixed bed retort and under fluid bed conditions, result in higher oil yield has not been addressed. Some of these retorting parameters might provide some kinetic advantages or they might enhance oil yield by the reduction of coking and cracking. Additionally, some combination of both of these explanations could be feasible as well as the possibility of the additional release of volatile matter from the shale by various retorting conditions. Comparison of information that has been obtained at the Institute for Mining and Minerals Research (IMMR) using a 1 1/2-inch diameter fixed bed retort and a 1 1/2-inch and 3-inch diameter fluid bed retort have provided insights to the mechanism of yield enhancement for eastern U. S. oil shales.

EXPERIMENTAL

Oil Shale

Several master batches of Kentucky oil shale were produced from bulk samples which were crushed, blended, sieved and riffled into representative aliquots for retorting. Samples were stored under argon in air-tight containers to retard aging prior to retorting. All samples used for this study were obtained from the Cleveland Member of the Ohio Shale and were mined in Fleming County, Kentucky. The master batch used for the 3-inch diameter fluid bed was 20-30 mesh particles and contained 12.2% carbon while the two samples of Ohio Shale used for the 1 1/2-inch fluid bed were 18-20 mesh particles and contained 11.6 and 11.0% carbon. These samples were also used in the fixed bed along with another sample containing 14.6% carbon.

Modified Fischer Assay and Fixed Bed Retorting Procedures

The bench scale fixed bed retort and the modified Fischer Assay procedures used at the IMMR have been described elsewhere (6, 7). Additional procedures used to operate the bench scale fixed bed retort under conditions of different heating rates, sweep gases, steam and vacuum are detailed in Rubel and Coburn (1).

Bench Scale Fluid Bed Retorts and Operating Procedures

A description of the 1 1/2-inch diameter fluid bed retort, the operating conditions and procedures and the product collection system used for this unit have been given in Rubel et al. (5). Similar information for the 3-inch diameter unit has been detailed in Carter et al. (4).

Retort Product Analysis

Gases from the fixed bed retort were analyzed on a Carle 311-H Gas Analyzer using Carle Application 357. Gases leaving the product collection apparatus from the fluid bed retorts were monitored on a Carle Gas Analyzer (Series SX-AGC) using Carle Application 397B. This enabled determination of off gas weight and carbon content. A Carlo-Erba 1106 Elemental Analyzer was used to determine C (total), H and N in the raw and spent shale and in the oil. Raw and spent shale and oil were also analyzed for moisture and ash (ASTM D3174). Raw and spent shale samples were subjected to thermogravimetric analysis on a Perkin Elmer TGS-2 for volatile matter and fixed

carbon determinations.

RESULTS AND DISCUSSION

Retort Products Distribution

Figure 1 compares the distribution of products for the fluid bed reactors versus the fixed bed retort operated under modified Fischer Assay conditions. Also given is the partitioning of carbon between spent shale, oil and gas. Material and carbon balances for both fluid bed retorts and the fixed bed retort were between 99 and 101%. The upper retorting temperature for all runs (both fixed and fluid bed) used for this comparison was between 533° and 550°C. Since gas yield has been shown to be dependent on upper retorting temperature (1, 5, 8) comparison of the distribution of products between spent shale, oil and gas can only be done between retorting runs with similar maximum temperatures. As can be seen from Figure 1, fluid bed retorting of Kentucky oil shale results in more oil and less gas yield in comparison to the same shale pyrolyzed in a fixed bed retort. In this case, oil yield weight was enhanced 36% and gas yield decreased 44%. These results are substantiated by the recovery of carbon in the products. Carbon recovered in the oil increased 33% while carbon in the gas decreased 17%. Also of significance is the fact that under fixed bed conditions 10% more carbon was recovered in the spent shale than under fluid bed conditions. As will be shown later, carbon recovered as coke is the likely source of this residual carbon.

Effect of Upper Retorting Temperature on Products

The most obvious effect of increasing the upper retorting temperature for both the fixed bed and fluid bed retorts is the substantial increase in gas make. Figure 2 is a plot of gas yield as percent of the raw shale versus maximum retorting temperature for the fluid bed units compared with fixed bed retorting at 12°C/min to different upper soak temperatures. Under both fixed bed and fluid bed retorting conditions there is a marked increase in the amount of off gas produced as the bed temperature is increased. However, the fluid beds produced considerably less gas than the fixed bed run at a similar retorting temperature. This is consistent with the fact that cracking of oil vapors in the fluid bed should be minimum due to their very rapid removal (0.6 sec) from the fluid bed retorts by the high sweep gas velocities required to maintain fluidization. Additionally, more cracking of oil vapor is expected as the bed temperature is increased under both retorting conditions which results in the observed increase in gases produced.

Evidence of oil cracking as the major source of the increased gas make is presented in Figure 3. In the 3-inch diameter fluid bed, a two fold increase in the amount of CH₄ (0.1 to 0.2 wt %) found in the off gas was noted as the bed temperature was increased from 470° to 530°C. This was accompanied by a shift in the composition of the gas as is shown in Figure 4. At a bed temperature of 478°C, the hydrocarbon off gas is 23 wt % CH₄ and 27 wt % C₄'s with intermediate amounts of C₂'s and C₃'s. At a bed temperature of 533°C, CH₄ composed 30 wt % of the gas and C₄'s 21 wt %. As the bed temperature increased, the hydrocarbon off gas composition shifted toward a higher concentration of the lower carbon number hydrocarbons. For comparison, the amount of CH₄ produced by a comparable sample of Ohio shale retorted in the fixed bed under modified Fischer Assay conditions was 0.3 wt % of the raw shale. This is greater than the amount produced (0.2 wt %) by the fluid bed at a comparable maximum temperature.

The information obtained from the off gas analysis implies that an optimum retorting temperature for maximum oil yield from Kentucky oil shales must be a balance between a temperature high enough to remove all volatile hydrocarbons from the shale but low enough to prevent excess cracking. This is verified by the oil yield results from the fluid bed retorts. Figure 5 indicates that there is a optimum bed temperature of 575°C for maximum oil recovery.

Effect of Bed Temperature on Volatile Matter Release

Figure 6 shows the effect of bed temperature on the release from the raw shale of volatile matter as determined by thermogravimetric analysis (TG). Included on this curve are points from both fixed and fluid beds. It is apparent that volatile matter release is dependent on the retorting temperature and not the method of retorting. Volatile matter by TG includes all volatile material (both organic and inorganic) in the shale. Also the amount of volatile matter removed from the raw shale includes the amount of organic carbon converted to fixed carbon. Therefore, the curve of bed temperature vs. volatile matter removed continues to increase beyond the point at which increased oil yield is no longer observed. However, the information of interest here is that both retorting technologies effect the same amount of volatile matter release, but the volatile matter goes to different products. This again implies that the reduction of cracking losses is the major factor in oil yield enhancement.

Oil Yield vs. Fixed Carbon Deposition

Further evidence for decreased cracking, as the major factor for increased oil yields

from Kentucky oil shales, is the relationship between oil yield and coking as monitored by the amount of fixed carbon in the shale determined by TG. Figure 7 gives the spent shale-to-raw shale fixed carbon ratio for several fluid bed runs at different bed temperatures compared to fixed-bed runs under modified Fischer Assay, inert sweep gas, steam and vacuum retorting conditions. In the fluid bed as bed temperature increases, CH_4 production increases, the percentage by weight of C_4 's in the hydrocarbon gas decreases, total gas make increases and fixed carbon (coke) deposition increases. All these factors point to increased oil vapor cracking with higher bed temperature. The difference in coke deposition between the fixed and fluid beds is dramatic; 30% more fixed carbon is deposited under Fischer Assay conditions. The relationship between fixed carbon deposition and oil yields from the fixed bed run under various conditions shows the dependence of oil yield enhancement on decreased coking. Inert sweep gas conditions produced an oil yield enhancement of 105% modified Fischer Assay with a 23% increase in fixed carbon whereas steam and vacuum runs produced between 115-120% Fischer Assay oil with only a 10% increase in the fixed carbon present in the spent shale over that found in the raw shale.

Comparison of volatile matter release (Figure 6), fixed carbon deposition (Figure 7) and oil yield provides an indication of the mechanism by which oil yield enhancement is obtained for eastern U. S. shale. For a fluid bed run at 475°C, less than maximum volatile matter is released but coke deposition is minimum with the resultant 120 wt % Fischer Assay oil yield produced. Fischer Assay conditions result in maximum organic volatile matter release and maximum fixed carbon deposition. Fixed-bed steam retorting again provides for maximum organic volatile matter release which, combined with moderate coking, produces an oil yield of approximately 120% of Fischer Assay. Fluidized bed retorting at 575°C was found to be optimum for maximum oil yields from the Ohio Oil Shale in this study. This allowed for maximum volatile release with minimum fixed carbon deposition and a resultant oil yield of 155-160 wt % Fischer Assay.

SUMMARY

Bench scale fluid bed and fixed bed retorting of Kentucky oil shale has provided evidence that for the small particle sizes used in this study increases in oil yield, which have been shown to be feasible for eastern U. S. shale, is primarily due to decreased cracking of oil vapors and that release of hydrocarbons from the shale depends on pyrolysis temperature and not the retorting technology used. The following information presented supports this statement: Under fluid bed conditions where oil vapors are rapidly removed from the retort more oil and less gas are produced than any fixed bed retorting conditions. Under fluid bed conditions, the proportion of CH_4 in the gas increases with increasing bed temperature at the expense of a lower proportion of C_4 's in the hydrocarbon gas. CH_4 produced under modified Fischer Assay conditions is greater than that obtained at a comparable bed temperature in the fluid bed. Oil yield from the fluid bed retorting of Ohio Oil Shale is maximized at a bed temperature of 575°C under retorting conditions used in this study. Removal of volatile matter as measured by TG from the shale depends on retorting temperature and not retorting method. Increases in the fixed carbon content of the spent shale relative to the raw shale are accompanied by decreased oil yields, increased gas make and increased CH_4 production in both fixed and fluid bed retorts. Under modified Fischer Assay conditions, 10% more carbon as determined by elemental analysis is left on the spent shale than a fluid bed run at the same maximum bed temperature; TG analysis of the spent shale indicates that this residual carbon is coke.

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FIGURE 1. MATERIAL AND CARBON BALANCES
FOR THE FLUIDIZED BEDS COMPARED
WITH MODIFIED FISCHER ASSAY

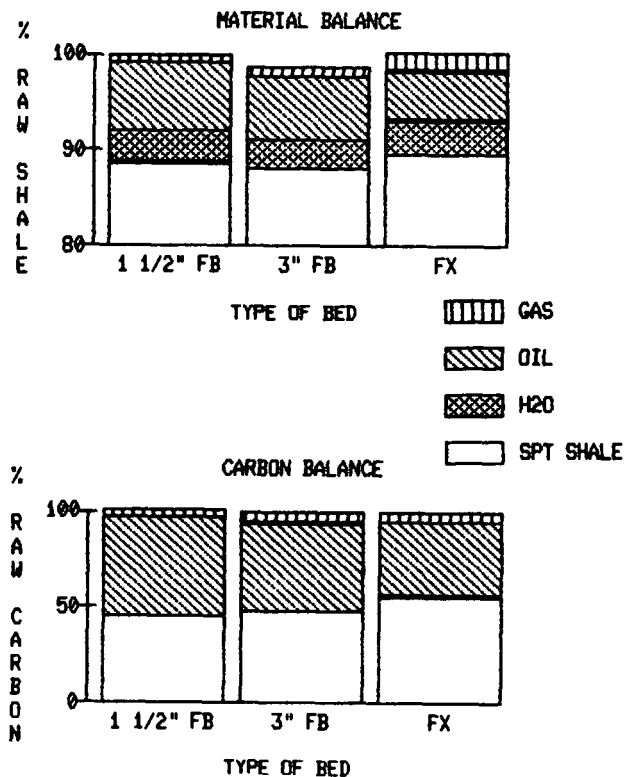


FIGURE 2. EFFECT OF TEMPERATURE ON GAS EVOLUTION

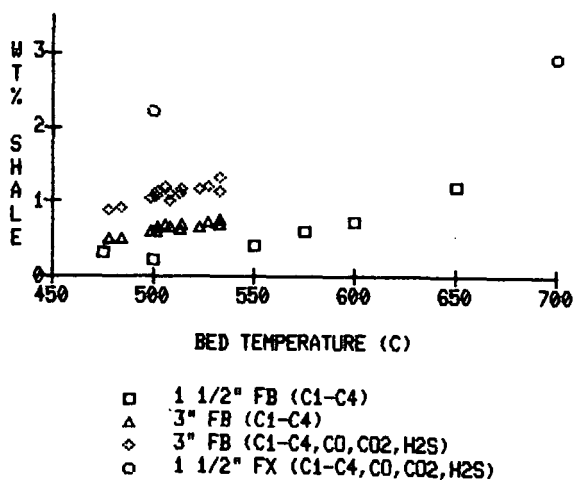


FIGURE 3. EFFECT OF BED TEMPERATURE ON METHANE EVOLUTION

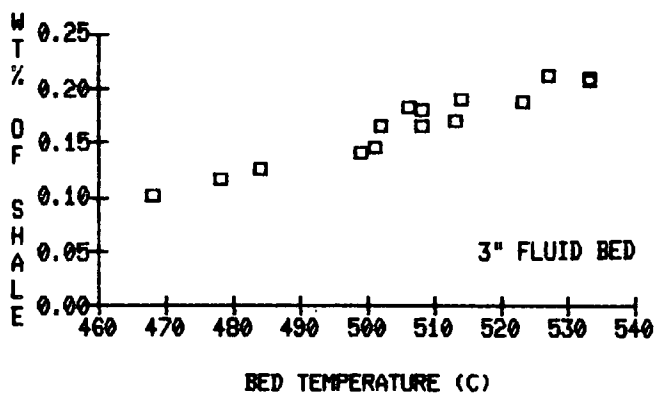


FIGURE 4. EFFECT OF TEMPERATURE ON HYDROCARBON GAS COMPOSITION

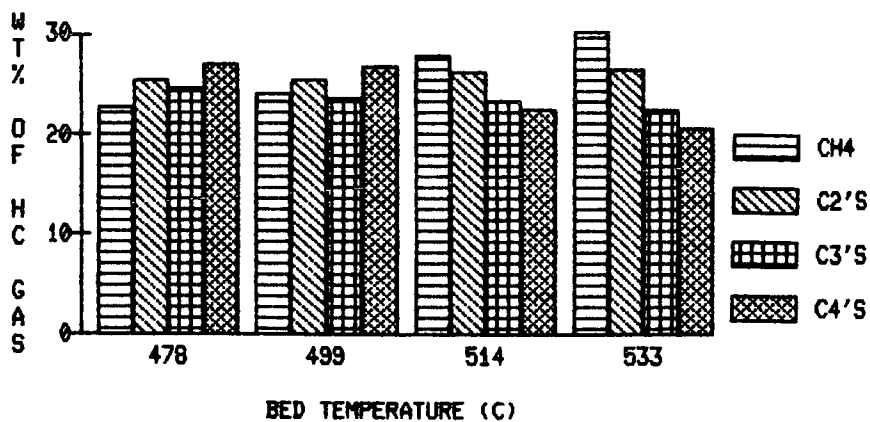


FIGURE 5. EFFECT OF BED TEMPERATURE ON OIL YIELD

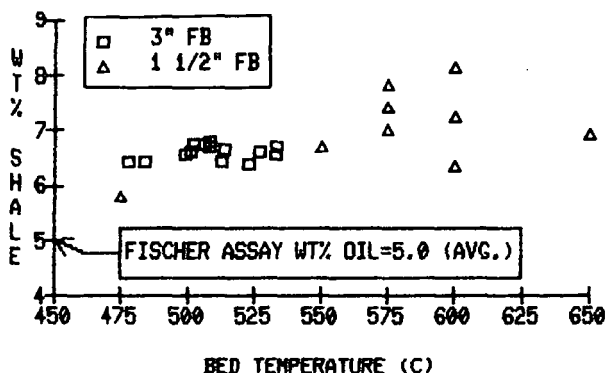


FIGURE 6. EFFECT OF BED TEMPERATURE ON VOLATILE MATTER BY TG REMOVAL IN THE FIXED AND FLUID BEDS

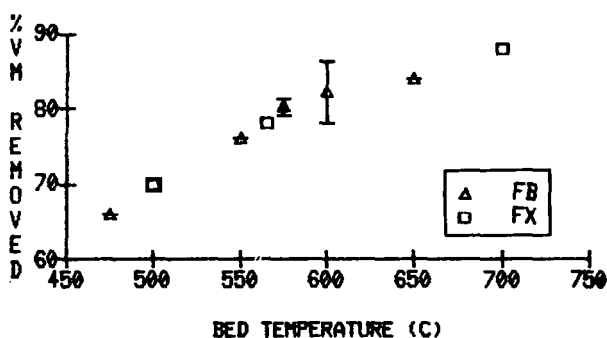
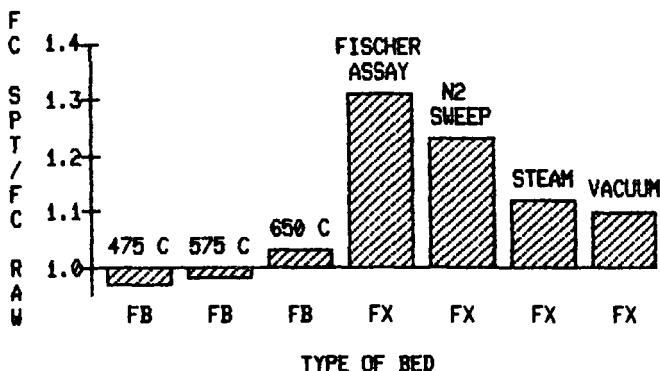


FIGURE 7. FIXED CARBON IN SPENT SHALE FROM DIFFERENT TYPES OF RETORTING CONDITIONS



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